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CONDENSATION

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April 3, 1952

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ABSTRACT

A method of analysis of non-condensable impurities in condensable gases or condensable impurities in non-condensable gases is presented. The method utilizes an arbitrarily added internal standard of the same type gas as the impurities. The precision of the method as used here is of the order of a few parts per hundred thousand.

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The determination of condensible impurities in non-condensable gases and the inverse, the determination of non-condensable impurities in condensable gases using condensation with liquid air as a means of concentrating the impurities is well known. Recently Shepherd, Rock, Howard, and Stormes (4) described the use of this method for determining condensible impurities related to smog in air, while Happ, Stewart and Brockmyre (3) used the method for the determination of condensible vapors in air.

In both of these papers the mass spectrometer sensitivity and the volume of the system were used to determine the amount of impurity present, relating it to the volume of sample collected. This method is quite satisfactory for the study of condensible gases in non-condensable gases provided the sample bulb volume is known and the pressures do not become too large. The method does not work as well, however, for non-condensable impurities in condensable gases where the volume cooled to liquid nitrogen temperature is somewhat dubious although it may be a small fraction of the total volume, and the fraction of gas mechanically entrapped in the large bulk of condensate is unknown.

To obviate this difficulty an internal standard has been introduced in concentration large enough to be measured easily in the total gas mixture but small enough so that after condensation the ratio of impurities to the standard is still reasonable. This eliminates errors due to mechanical entrapment and temperature variations. Internal standards have been used in mass spectrometric analyses before. Grosse, Hindin and Kirshenbaum (2) used an internal standard of O^{18} , N^{15} , or C^{13} for the determination of oxygen, nitrogen or carbon in the elementary analyses of organic materials, while Thomas and Sigfried (5) used an internal standard of benzene in the analysis of liquids. In the work given here, neon was used as an internal standard for non-condensable gases while sulfur dioxide was used as an internal standard for condensable gases. Any gas not a component of the mixture can be used for the standard, but it is convenient to use one with an isolated peak of considerable sensitivity.

Procedure

All gases used were of the highest purity available and all condensable gases were distilled three times in a vacuum, pumping on the gas with a fast oil pump after each distillation. All gases were mass spectrometer checked for purity. Where the impurities were non-interfering, e.g., 0.2% argon in oxygen, impurity peaks were considered part of the gas spectrum. The CO used was only 97.5% pure, containing both oxygen and nitrogen, and these impurities were added to the O_2 and N_2 contents respectively.

Known mixtures were made up in a 500 ml gas bottle shown in Fig. I, A. It has a fine sintered disc inlet sealed onto the side and covered with mercury. This bottle must of course be maintained upright and the disc covered with mercury at all times. The volume of this bottle was accurately measured by expansion comparison to a standard bottle calibrated by weight of water contained. The stopcock used on both this bottle and the subsequent mixing bottle were high vacuum stopcocks of the hollow plug type which eliminated trapping of unequilibrated gas in a stopcock bore.

For the preparation of compositions containing known gas impurities, the bottle was evacuated to better than 10^{-5} mm mercury as measured on a McCleod gage. The non-condensable gases were then added through the sintered disc using calibrated gas pipettes of the type described by Charlet. (1) After the impurity gases were added, the main component was added from the vacuum system and the total pressure measured on a manometer. The stopcock to the system was left open only a few seconds after the introduction of the main component to prevent diffusion of the impurities into the system yet long enough for pressure equilibration in the two parts of the system. This gas mixture was allowed to sit overnight after warming and cooling spots on the side of the bottle to aid in mixing of the gas components. For making mixtures containing traces of condensable gases in non-condensable, the condensable gases were added as liquids through the mercury disc from calibrated precision capillary dippers (1) of suitable volume. The

non-condensable gas was then added from the vacuum system as before.

After composition equilibration of the gases in the 500 ml gas bottle, the gases were mixed with the internal standard in a mixing bulb of about 100 ml capacity shown in Fig. IB. The internal standard was added to the mixing bulb to a pressure of 8 to 10 mm and the gas to be analyzed was then quickly added to the equilibrium pressure between the two bulbs. The mixing bulb was closed off, heated on one side for a few moments to thoroughly mix the gases, and then analyzed with the mass spectrometer. The total gas was run first and then the mixture frozen and the non-condensibles run or conversely, the non-condensibles pumped off and the condensibles run after warming.

The spectrometer used was a Consolidated Engineering Corporation model 21-102 converted to model 21-103 except for the inlet system. The spectrometer was operated in accordance with the manufacturer's recommendations. In running the total gas, only the ratio of main component to the internal standard was determined, so the internal standard peaks (Ne masses 20, 22, and SO₂ mass 64) were run at 5 times sensitivity by increasing the electron emission while the rest of the spectrum was scanned at normal emission. When running the separated fractions, all peaks except the internal standard peaks were run at 5 times sensitivity. This allowed the ratios of the internal standard to the minor components to be obtained with considerable accuracy. The analyses of the mixture spectra were performed in the usual manner. For mixtures containing CO and N₂, the contributions to the peaks 12, 14, 16, and 28 were adjusted to give the best fit to the observed residual spectrum on all these peaks after all other components were removed.

Discussion

The results on several synthetic mixtures are shown in Tables I and II. It is seen that the precision of the method is of the order of a few parts per hundred thousand, and the unknown mixture V, which was divided into two parts and run independently, including separate neon additions, on separate days, illustrates that the reproducibility is better than the absolute precision. For non-condensable impurities in condensable gases the least precision is exhibited by carbon monoxide. This is probably related to the background at mass 28 on the instrument, due apparently to CO from the filament which varies in amount with the gas composition being analyzed. Methane in SO₂ was also low and this may be related to the solubility of methane in solid SO₂ which would lead to erratic results in this gas. It might be mentioned that in mixture II, the propane used, (Phillips Petroleum Co., research grade), contained a trace of methane which gave very erratic results on both the pure propane blank and the mixture. The methane spectrum in this case was simply subtracted out and not considered in the analysis. The absolute accuracy of condensibles in air is about the same as that of non-condensibles in condensable gases. In Table II, all condensible impurities are low by a few parts per hundred thousand due probably to adsorption on the glass disc and the walls of the mixing chambers resulting in the actual composition being lower than calculated from the dipper volumes.

As used here the sensitivity of the method of analysis by use of an internal standard and liquid air separation seems to be limited to a few parts per hundred thousand separable impurity. This limitation

is imposed by the range of sensitivities of the components. The sensitivity might be pushed to a few parts per million by using the available decreased sensitivity of a factor of 10 for the main component and internal standard in the two respective runs, but this has not been done in the present work.

This work was done under the auspices of the Atomic Energy Commission. The author wishes to thank Mr. Laurin Tolman for aid in running the samples on the mass spectrometer.

Table I

Non-condensable Impurities in Condensable Gases

<u>Mixture I</u>	Added	Found	Δ
CO ₂	99.66%	99.67%	
Air	0.127	0.129	+0.002
CO	0.208	0.197	-0.011
Ne - Internal standard			
<u>Mixture II</u>			
Propane	99.74%	99.74%	
He	0.112	0.114	+0.002
H ₂	0.112	0.117	+0.005
O ₂	0.034	0.032	-0.002
Ne - internal standard			
<u>Mixture III</u>			
CO ₂	99.45%	99.46%	
O ₂	0.111	0.109	-0.002
N ₂	0.222	0.222	0.000
CO	0.215	0.205	-0.010
Ne - internal standard			
<u>Mixture IV</u>			
SO ₂	99.46%	99.50%	
O ₂	0.036	0.034	-0.002
N ₂	0.037	0.045	+0.008
CO	0.116	0.102	-0.014
H ₂	0.205	0.198	-0.007
CH ₄	0.114	0.086	-0.028
A	0.035	0.034	-0.001
Ne - internal standard			
<u>Mixture V (unknown)</u>			
	Anal I	Anal II	
CO ₂	99.847%	99.842%	
CO	0.102	0.102	
O ₂	0.017	0.018	
N ₂	0.034	0.038	
Ne - internal standard			

Table II

Condensible Impurities in Non-condensable Gases

<u>Mixture I</u>	Added	Found	Δ
Dry CO ₂ free Air	99.62%	99.66%	
Ethanol	0.087	0.072	-0.015
Acetone	0.032	0.028	-0.004
Ethyl Ether	0.048	0.043	-0.005
n-Pentane	0.084	0.074	-0.010
Ethyl Bromide	0.130	0.125	-0.005
SO ₂ - internal standard			

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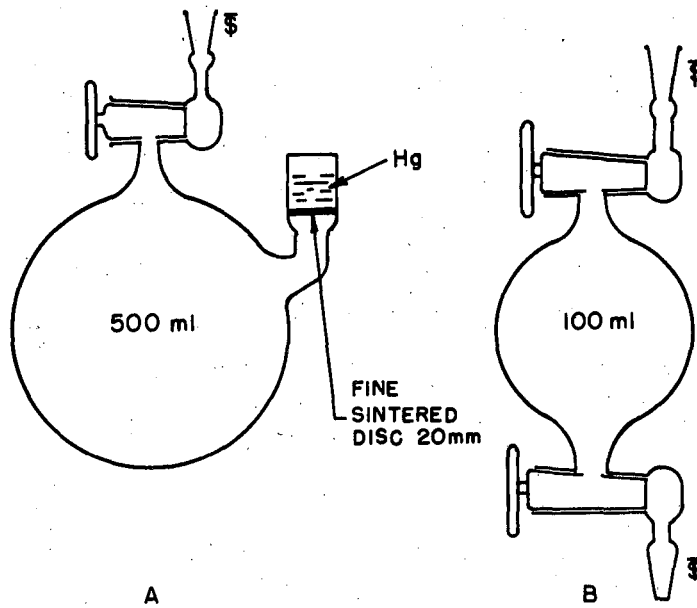


FIG. 1

- A) GAS BOTTLE FOR MAKING MIXTURES
- B) MIXING BULB FOR ADDING INTERNAL STANDARD GAS

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Fig. 1